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(54) CONTINUOUS PRODUCTION OF DICARBOXYLIC ACIDS AND ANHYDRIDES

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved process for the continuous production of dicarboxylic acids and anhydrides, particularly of phthalic anhydride and maleic anhydride, by the oxidation of aromatic hydrocarbons, particularly of benzene, o-xylene or naphthalene, with oxygen or a gas containing free molecular oxygen in contact with a fixed-bed catalyst containing vanadium pentoxide at from 350° to 500°C in the gas phase, and, if desired, conversion of the initially produced anhydride into the acid.

This process, in so far as it does not relate to the improvements herein described and claimed, is generally known and is carried out commercially in many variants, usually occasioned by the catalyst.

It is common to all these variants that a mixture of air (as a gas containing free molecular oxygen) and the hydrocarbon to be oxidized is passed through a large number of tubes arranged in a reactor and containing the fixed-bed catalyst. The outer walls of the tubes are kept at the reaction temperature appropriate to the system in question by means of a flowing heat exchange medium, usually a salt melt.

All variants have the disadvantage that troublesome by-products are formed which can only be separated from the desired products with difficulty. These by-products, particularly aldehydes or phthalide in the production of phthalic anhydride, impair the quality of the main products even in very low concentration.

The problem of preventing the formation of by-products or at least substantially suppressing their formation has not hitherto been solved satisfactorily. If the entire reaction is carried out under more drastic conditions—for example at a higher temperature, with more effective catalysts and/or with longer contact times—the amount of by-products is decreased as would be expected, but the yield of the main product also declines so that the overall disadvantage is greater.

It is known that the temperature maximum ("hot spot") occurs in the first third of the catalyst bed after entry of the mixture of air and hydrocarbon. An attempt is made to keep the temperature of the salt melt at from 390° to 420°C so that the hot spot does not exceed 500°C.

When the space velocity is low, for example 2000 to 4000 m³ of air per hour, pure products are obtained. To ensure a long life of the catalyst it is advantageous to choose a temperature maximum of from about 460° to 475°C. Often however pure products are not then obtainable.

If on the other hand the space velocity is high (more than 4000 m⁴ of air per hour) it is necessary to raise the temperature of the salt bath in order to achieve a high spot spot which is usually above 500°C. There is then a marked combustion, a fall in yield and a shortening of the life of the catalyst.

It is thus evident that a mere increase in temperature involves too serious disadvantages.

It is the object of this invention to suppress as much as possible the formation of by-products in the production of dicarboxylic acids and anhydrides by the above-mentioned method.

We have found that contrary to expectation the said disadvantages are reduced or avoided by conducting the reaction so that

during the contact time the reaction mixture is exposed to more drastic reaction conditions, after it has passed the first third of the total catalyst bed, which result from or are equivalent to a rise in the temperature of the heat exchange medium surrounding that section of the bed in which the said more drastic reaction conditions are applied of from 5° to 50°C, particularly from 10° to 45°C.

After the first third, preferably half, of the reactor tubes, more drastic reaction conditions may be set up by the following measures which may be used alone or in any combination:

(a) by raising the temperature of the heat exchange medium in one or more stages. This measure requires separate circulating systems of the heat exchange medium and serves inter alia for preliminary tests for the exact quantitative appraisal of the necessary more drastic conditions;

(b) by increasing the effectiveness of the catalyst in the direction of flow of the reaction mixture. The effectiveness of the catalyst increases with the content of vanadium pentoxide so that all that is necessary is to charge the reaction tubes successively in the direction of flow with catalysts having increasing contents of vanadium pentoxide;

(c) by prolonging the contact time of the gas by using tubes which are longer than the hitherto conventional length of tubes, namely about 3 meters, for example up to 150% of the conventional length (preferably about 4 meters), or by using tubes of greater internal diameter, for example about 1.25 times to twice the internal diameter;

(d) by decreasing the transfer of heat from the interior to the exterior of the tubes by providing them with a thermal insulator;

(e) by an after-reaction in a second reaction chamber at higher temperature and/or with more effective catalysts and/or for longer contact times.

All these measures may be intensified by allowing the heat exchange medium to flow, not countercurrent as hitherto exclusively customary, but in the same direction as the reaction gas.

All types of nested tube reactor are suitable for carrying out the process according to this invention, in method (a) after the chamber for the heat exchange medium has been subdivided into two or more zones, in method (b) direct, in method (c) after the tubes and consequently the reactor have been prolonged or their original cross-section widened by 50 to 100% (conical tubes) continuously or in one or more stages, and in method (d) after internal or external insulation of the tubes in a layer thickness of from 0.5 to 2 mm, for example with asbestos or an air jacket, the insulating material being held in place by a jacket tube.

When method (b) is chosen, either the layer thickness of the catalytic composition of the supported catalyst may be increased by up to 150 to 500% of the original thickness (regarded as 100%) or by increasing the surface area of the active material, or by increasing the content of vanadium pentoxide at a constant bed thickness.

If the catalyst contains only a few percent, for example 1 to 6%, of vanadium pentoxide, the amount may be increased by 5 to 500%, advantageously from 50 to 300%, of the original amount. In cases where the vanadium content is higher, only a modest increase, for example by from 5 to 80%, is made.

In the same way a carrier which is provided with from 3 to 10% of a catalytic composition may be coated in subsequent zones with an amount which is up to 20 to 100% larger.

A plurality of successive reactors may be used which have catalysts having increasing vanadium content.

Generally the temperature following the hot spot drops by from 60° to about 110°C after only 45 to 100 cm in a catalyst zone of 3 metres depending on the amount of mixture of air and hydrocarbon passed through. This drop may be delayed for a length of from 1 to 2.50 meters by means of measures (a) and (d).

For after-reaction in accordance with method (e) it is advantageous to use a shaft furnace because the reaction conditions therein can be regulated so that cooling is unnecessary. More than one tube furnace can be connected with one shaft furnace.

A downstream shaft furnace has the advantage that oxidation in the tube furnaces can be carried out with high throughput, for example 8000 to 12000 m³/hour of air and 40 to 60 g/m³ of hydrocarbon and with a low hot spot of about 460° to 470°C, thus ensuring a long catalyst life.

The shaft furnace may be filled with particles of catalyst which have a smaller diameter, or advantageously a larger diameter, or a larger or smaller bed thickness than that in the tube furnace. Sometimes it is advisable to cool the gas issuing from the tube furnace before it enters the shaft furnace to a lower temperature, for example from 280° to 350°C, by a heat exchanger.

It is common to all the process variants (a) to (d) that the reaction in the first third of the tubes in the reactor is the same as in the prior art methods and that the deviations following the same added according to this invention are relative deviations in relation to the basic method in question. An absolute characterization of the improvement in the process according to this invention—for example by specifying the catalyst com-

position according to method (b)—is therefore not possible. It is also unnecessary however because the application of the new teaching to concrete embodiments requires merely a few simple preliminary experiments, advantageously using method (a). The lower the hot spot chosen, the greater the rise in temperature which is necessary.

The new teaching means in general that the temperature drop after the temperature maximum (hot spot) in the first third of the tubes is moderated: the temperatures are measured in the interior of the tubes, i.e. in the catalyst.

Particularly important examples of oxidation reactions in which yield and purity of the desired product can be improved by the process according to this invention are the partial oxidation of naphthalene and especially of o-xylene into phthalic anhydride and also of 1,2,4-trialkylbenzenes or β-alkylnaphthalenes into trimellitic acid or anhydride and of benzene into maleic anhydride with air as the gas containing free molecular oxygen.

In the case of the production of phthalic, trimellitic and maleic anhydrides, it is mainly the formation of compounds having phthalide or gamma-hydroxycrotonolactone structure which is suppressed. Phthalide, as a by-product of phthalic anhydride, is mainly troublesome as a monofunctional compound because it causes chain termination in polycondensations of phthalic anhydride with bifunctional alcohols. Moreover other products which are not thoroughly oxidized, such as aldehydes, impair the heat color test.

The mixtures of air and hydrocarbon may have the usual composition, from about 40 to 60 g/m³ (STP); it is preferred to keep below the explosion limits.

Vanadium compounds which are dissolved in a melt of ammonium thiocyanate are suitable for the production of the fixed-bed catalysts. Supported catalysts containing mainly vanadium pentoxide on inert substances are advantageously used. The vanadium may be used in the form of oxalates, formates, acetates, chlorides, sulfates or as ammonium salts, amine salts, amidinee salts or as esters of vanadic acid or as complex salts of organic or inorganic acids.

It is preferred to use nonporous material having an internal surface area of 4 m² per gram as the carrier. Porous substances having an internal surface area of from about 30 to 400 m² per gram may also be used. The following substances are suitable: porcelain, natural or synthetic silicates such as aluminium, magnesium, zinc or zirconium silicate or silicon carbide, magnesium oxide, pumice, silicic acid, quartz, titanium dioxide (anatase or rutile), cerium oxide, aluminas or mixtures of these substances. The carrier may be sintered or fused prior to use, as for example silicates or aluminas. The carrier

is generally used in the form of spheres having a diameter of from 4 to 12 mm. It is also suitable as granules, pellets, cones, rings or stars. The carrier substance may also be mixed with the vanadium compound and shaped. Supported catalysts having a particle diameter of from about 4 to 12 mm and containing vanadium pentoxide and titanium dioxide in the active compositions are particularly suitable. These catalysts, which are outstandingly suitable for the production of phthalic acid from o-xylene and naphthalene are described for example in British Patent Specification No. 1,140,264. The active composition is advantageously composed of from 1 to 25%, preferably from 2 to 15%, by weight of vanadium pentoxide and 99 to 75%, preferably 98 to 85%, by weight of titanium dioxide with or without traces of other metal compounds. The proportion of the active composition to the total weight of catalysts should be from about 1 to 12%, and the proportion of vanadium pentoxide should preferably not exceed 3% by weight and is advantageously from 0.05 to 2%. As regards methods (b), these statements concerning the catalyst apply to the catalyst employed in the initial part of the bed.

Compounds of zirconium, lithium, aluminum and phosphorus, the latter advantageously as phosphoric acid, in an amount of from about 0.05 to 50%, particularly from 0.05 to 20%, preferably from 0.05 to 5%, by weight have proved to be suitable as further additives to the catalytic composition. Compounds of tin, chromium, molybdenum, tungsten, silver, manganese, iron, nickel and cobalt may also be added in an amount of from 0.2 to 25%, particularly from 0.2 to 15%.

Depending on the activity, the catalysts are placed in reaction tubes having a length of from 2 to 6 meters and an internal diameter of from 18 to 40 mm, provided a greater cross-section is not necessary according to method (c) after the first third. About 3500 to 12,000 liters of the mixture of hydrocarbon and air is passed through the reactor per reaction tube per hour. The gas mixture leaving the reactor is processed as usual.

Salt melts, for example melts of mixtures of potassium nitrate and sodium nitrate are particularly suitable as heat exchange media. These melts are used in the conventional methods so that no further details are needed.

It is remarkable that the further reaction according to the invention does not proceed at the expense of the total oxidation of the main product, but that the byproducts of a lower oxidation state are oxidized to the acids or anhydrides.

The invention is illustrated by the following Examples.

EXAMPLE 1

In order to prepare phthalic anhydride from o-xylene, a hot mixture (at 140°C) of 5100 m³ of air and 200 g of 95% o-xylene is passed per hour through an iron tube having a length of 1 meter and an internal diameter of 25 mm filled with a supported catalyst. A salt melt at 385°C which is cooled outside the tube is passed countercurrent to the gas mixture. Immediately behind the reactor there is a second tube filled with the same catalyst and having a length of 2 meters and an internal diameter of 25 mm. This tube is situated in a salt melt at 410°C.

The yield of pure distilled phthalic anhydride is 115% by weight (based on pure o-xylene). The phthalide content is 0.004% by weight.

For the preparation of the catalyst, 2500 g of 6-mm porcelain spheres are sprayed in a coating drum heated to 300°C with 400 g of an aqueous suspension containing 42.5 g of formamide, 18.7 g of oxalic acid, 8.5 g of vanadium pentoxide, 133 g of anatase and 1 g of acid ammonium phosphate (NH$_4$H$_2$PO$_4$). The proportion of active composition in the supported catalyst is 4% by weight. The proportion of vanadium pentoxide is 0.24% by weight. The average thickness of the bed of catalyst composition is about 0.05 mm. After the coating operation, the catalyst is heated for two hours in a stream of air at 450°C.

EXAMPLE 2

To prepare phthalic anhydride from o-xylene, a mixture of 6.8 m³ of air and 270 g of 98% o-xylene is passed per hour through an iron tube filled with supported catalyst to a height of 3 meters and an internal diameter of 25 mm which is in a salt bath at a temperature of 388°C.

The first half of the tube in the direction of flow is charged with a supported catalyst (I) containing vanadium pentoxide and containing 6% of its weight of active composition, and the catalyst (II) in the second half has 8% of active composition.

The yield of pure (already distilled) phthalic anhydride is 110.5% by weight based on pure o-xylene (i.e. 100 kg of pure o-xylene would yield 110.5 kg of phthalic anhydride) and the content of phthalide is less than the detectable limit.

By working under the said conditions but only with catalyst (I), the phthalide content is 0.07%.

When catalyst (II) alone is used, the yield of phthalic anhydride falls to 109% by weight.

Transition from catalyst (I) to catalyst (II) corresponds to an increase in the salt bath temperature of from 388° to 420°C in the zone of catalyst (II).

The active composition of the supported catalysts used consists of about 6% of vanadium pentoxide and 94% of anatase. It is applied in the form of a suspension of 350 parts by weight of water, 42.5 parts of formamide, 18.7 parts of oxalic acid, 8.5 parts of vanadium pentoxide and 133 parts of anatase to magnesium silicate spheres having a diameter of 7 mm which are heated to 300°C. The active composition is fixed on the carrier by heating in a current of air for three hours at 450°C.

EXAMPLE 3

For the production of phthalic anhydride from o-xylene, a mixture of 8.5 m³ of air and 340 g of 98% o-xylene is passed per hour through an iron tube charged with supported catalysts to a height of 2.2 meters and which is situated in a salt bath heated to 400°C.

The first 1.2 meters of the tube in the direction of flow has an internal diameter of 25 mm and the internal diameter of the remaining 1 meter is 45 mm. In the wider section of the tube the residence time of the gas is about three times the residence time in a tube of equal length and having an internal diameter of 25 mm.

The catalyst used is catalyst (I) from Example 2.

The yield of pure (already distilled) phthalic anhydride is 109% by weight and the content of phthalide is below the detectable limit.

By using the same conditions but a tube having an internal diameter of 25 mm throughout, the yield of phthalic anhydride is 107% by weight and the phthalide content is 0.5%.

The use of a tube having an internal diameter of 45 mm throughout is not possible for reasons of heat removal.

The transition of the tube diameter from 25 mm to 45 mm corresponds to an increase in the salt bath temperature from 400° to 430°C for the zone of the wider tube.

EXAMPLE 4

For the production of phthalic anhydride from o-xylene, a mixture, preheated to 140°C, of 8.5 m³ of air and 340 g of 95% o-xylene is passed per hour through an iron tube filled with supported catalysts to a height of 3 meters and having an internal diameter of 25 mm which is situated in a salt bath heated to 410°C.

This tube contains (from the length of 1 meter in the direction of flow) a piece of tubing having a length of 1.6 meters and a thickness of 0.5 mm. A layer of asbestos 1 mm in thickness is provided as insulation between the two pieces of tube.

The hot spot is 490°C. After this the temperature falls to 478°C. In the insulated

portion the temperature rises to 483°C and falls at the end of the insulation to 423°C. A temperature of 410°C is set up at the exit from the tube.

Catalyst (I) from Example 2 is used.

The yield of pure phthalic anhydride is 109% by weight and the content of phthalide is 0.005%.

When the tube is not insulated, 107% by weight of phthalic anhydride and 0.5% of phthalide are obtained. When a mixture of 6800 m³ of air and 270 g of 95% o-xylene is used, a salt bath temperature of 400°C is used. The hot spot has a temperature of 480°C. Thereafter the temperature falls to 467°C. In the insulated portion of the tube it rises to 474°C and falls to 417°C. In the following noninsulated portion, a temperature of 400°C is set up. The yield of pure phthalic anhydride is 110.5% by weight. The phthalide content is 0.005% by weight.

The transition from the noninsulated portion to the insulated portion of the tube corresponds to an increase in the salt bath temperature from 400° to 420°C.

EXAMPLE 5

For the production of phthalic anhydride from o-xylene a mixture, heated to 150°C, of 8.5 m³ of air and 340 g of 98% o-xylene is passed per hour through an iron tube having a length of 1.5 meters and an internal diameter of 25 mm which is situated in a hot salt bath at a temperature of 380°C and which is filled with supported catalyst. A hot spot forms within the first third; it is at 470°C.

The reaction gas passes into an attached tube having an internal diameter of 100 mm and a height of 200 mm. This is insulated externally.

The first tube is filled with magnesium silicate spheres having a diameter of 6 mm which are coated with 4% of the active composition of Example 2. In the attached unheated tube there are 1250 ccm of magnesium silicate spheres having a diameter of 5.4 mm which are coated with 6% of the active composition described in Example 2.

The yield of pure distilled phthalic anhydride is 111% by weight. The content of phthalide is below the detectable limit.

Transition from the 25 mm tube into a wider vessel corresponds to an increase in the salt bath temperature from 380° to 415°C, the last-mentioned temperature being measured in a 25 mm tube attached to the first tube which contains the said 1250 ccm of catalyst.

EXAMPLE 6

For the production of phthalic anhydride from naphthalene, a mixture heated to 150°C of 6.8 m³ of air and 290 g of naphthalene is passed per hour through an iron tube filled with a supported catalyst, having a length of 3 meters and an internal diameter of 25 mm, and situated in a hot salt bath at 375°C. The upper half of the tube is provided with magnesium silicate spheres having a diameter of 6 mm which are coated with 3% of the composition described in Example 1, whereas the lower half contains the same spheres but containing 6% of the composition described in Example 1. The mixture flows downward through the tube. Pure distilled phthalic anhydride is obtained in a yield of 111% by weight. The product is devoid of naphthoquinone.

Transition from the upper catalyst to the lower catalyst corresponds to an increase in the salt bath temperature from 375°C to 395°C in the zone of the lower catalyst.

WHAT WE CLAIM IS:—

1. A process for the continuous production of dicarboxylic acids and anhydrides by oxidation of aromatic hydrocarbons with oxygen or a gas containing free molecular oxygen in contact with a fixed-bed catalyst containing vanadium pentoxide at from 350° to 500°C in the gas phase and, if desired, conversion of the initially produced anhydride into the acid, wherein the reaction mixture during the contact time and after it has passed the first third of the total catalyst bed is exposed to more drastic reaction conditions which result from or are equivalent to a rise in the temperature of the heat exchange medium surrounding that section of the bed in which the said more drastic reaction conditions are applied of from 5° to 50°C.

2. A process as claimed in claim 1 wherein the reaction mixture is exposed to the more drastic reaction conditions after having passed through half of the total catalyst bed.

3. A process as claimed in claim 1 or 2 wherein the content of vanadium pentoxide in the catalyst is increased by from 5 to 500% of the original amount (regarded as 100%) to provide more drastic reaction conditions, provided that if the original amount exceeds 6% by weight the increase is not more than 80% of the original amount.

4. A process as claimed in any of claims 1 to 3 wherein the thickness of the layer of active composition in the supported catalyst is increased by up to 150 to 500% of the original thickness (regarded as 100%) to provide more drastic reaction conditions.

5. A process as claimed in any of claims 1 to 4 wherein the residence time of the reaction gas is increased by using a longer tube to provide the more drastic reaction conditions.

6. A process as claimed in any of claims 1 to 5 wherein the residence time of the

reaction gas is increased by using a wider tube to provide the more drastic reaction conditions.

7. A process as claimed in any of claims 1 to 6 wherein the more drastic reaction conditions are produced by decreasing transfer of heat through the tube.

8. A process as claimed in any of claims 1 to 7 wherein reaction under the more drastic reaction conditions is carried out in a shaft furnace.

9. A process as claimed in any of claims 1 to 8 wherein a globular supported catalyst is used both for the initial part of the bed and for the part of the bed subjected to the more drastic reaction conditions, the globules being coated with an active composition which contains from 1 to 25% by weight of vanadium pentoxide and 99 to 75% by weight of titanium dioxide, the content of vanadium pentoxide not being more than 3% by weight of the total amount of catalyst.

10. A process as claimed in any of claims 1 to 9 wherein the temperature of the heat exchange medium is kept at from 390° to 420°C during the first part of the reaction in the tube reactor.

11. A process as claimed in any of claims 1 to 10 wherein the heat exchange medium in the reactor flows in the same direction as the reaction gas.

12. A process for the continuous production of dicarboxylic acid anhydrides as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

13. Dicarboxylic acids and anhydrides when obtained by the process claimed in any of claims 1 to 12.

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